PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
VANDEVOORDE, P. et al.

Serial No.: 09/444,968
Filing Date: November 22, 1999

For: COATING COMPOSITION BASED ON A HYDROXY GROUP-CONTAINING FILM FORMING POLYMER, A POLYISOCYANATE COMPOUND AND A DIOL

: Docket: ACO2587P1US

: Examiner: Bissett

: Group Art Unit: 1773

Assistant Commissioner of Patents
Washington, D.C. 20231

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Angelique [signature]

February 10, 2003

RESPONSE

Sir:

In response to the Office Action of August 8, 2002, Applicants provide the following remarks for entry in this application. This response is filed in accordance with 37 CFR 1.111.

Presently, claims 1-17 are pending, though claims 7-11 and 13-17 have been withdrawn from consideration.

As a first matter, Applicants acknowledge and thank the Examiner for allowing claim 6.

Before addressing the specific rejections involved in this case, Applicants would like to clarify some things with regard to the Examiner's assertions in the present office action.

The Examiner appears to erroneously take the position that a claim directed towards a composition comprising components would include a composition comprising the reaction products of said components. More particularly, the Examiner alleges that a composition comprising a diol and a

<u>diisocyanate would include a composition comprising th polyurethan being the reaction product of said components.</u>

Applicants are truly perplexed with regard the Examiner's statements regarding Ho. Under the standard of anticipation, Ho does not disclose the present invention. Ho must contain within its four comers a sufficient description to enable one to practice the invention of the rejected claims without undue experimentation or inventive skills. *Akzo N.V. v. U.S. Intern. Trade Com'n*, 1 USPQ2d 1241, 1245 (Fed. Cir 1986). As set forth previously and as described by the Examiner, Ho does not anticipate the present invention.

The interpretation of the claim language in Ho **cannot** be expanded to include any and all possible materials the words *might* read on, only the functional equivalents of what is disclosed in the specification. *In re Donaldson Co., Inc.*, 29 USPQ2d 1845 (CAFC 1994). Nothing in Ho discloses the diol and the diisocyanate <u>as the coating composition</u> .

If there is not a reasonable certainty that the claimed subject matter will necessarily result, a rejection based on anticipation must fail. *In re Brink*, 164 USPQ 247, 249 (CCPA 1970). In the present instance, nothing in Ho discloses the coating composition of the present invention having AS SEPARATE (NON REACTED) components a diol and diisocyanate....and nothing in the Ho examples results in a coating composition having AS SEPARATE (NON REACTED) components, a diol and diisocyanante.

A first important difference between a composition comprising a diol and a polyisocyanate and a composition comprising a polyurethane lies in their respective viscosities. On the one hand, monomeric diols and isocyanates are usually low in viscosity and serve as diluents for a coating composition. On the other hand, polymers can be highly viscous or even be solid, depending on the molecular weight for a given polymer (J. Bentley, G.P.A. Turner, Introduction to Paint Chemistry, 4th Edition, Chapman & Hall, 1998, p. 131, first full paragraph) (copy attached). The viscosity of a coating composition governs its application properties (Bentley et al., p. 93, last paragraph, p. 94, 1st paragraph) (copy attached). In the present case and as set forth above, Applicants respectfully

requ st that it the Examiner maintains that the Ho reference anticipates the present inv ntion, sh specifically set forth, within th confines of a coating composition, how Ho could be applied to a substrate in the intermediary stage.

A second difference between a composition comprising a diol and a polyisocyanate and a composition comprising a polyurethane lies in storage stability. A composition comprising a diol and a polyisocyanate increases in viscosity after mixing due to the reaction of the components and the composition thus has a pot life (Table 3 on p. 17 of the application). Conversely, a polyurethane is depleted of isocyanate groups and is storage stable for a long period of time without any change in properties. A skilled person is aware of the importance pot life has as a property of two pack paints (Bentley et al., p. 100, paragraph titled "Drying by chemical reaction between ingredients in the paint").

A third difference is that a diol is a compound of a specified formula characterized by a special arrangement and connectivity of atoms, and by the presence of functional groups, namely two hydroxyl groups. In the reaction with polyisocyanate the hydroxyl groups are converted to urethane groups. In the light of the foregoing explanation it should be clear that the urethane resin thus prepared no longer comprises the diol as a compound with hydroxyl groups, but a polymer having urethane groups.

Thus, a skilled person is very well aware of the differences between a composition comprising a diol and a polyisocyanate and a composition comprising a polyurethane. For coating compositions in particular, these differences are of great importance. Accordingly, **a skilled person will not interpret a claim reading on a coating composition comprising a diol and a polyisocyanate as including a coating composition comprising the polyurethane being the reaction product of said diol and said polyisocyanate.**

Specifically, claims 1, 2, 4, 5, and 12 stand rejected for alleged anticipation by Ho. Applicants respectfully maintain their traverse of this rejection for at least the reasons set forth in previous responses, the remarks made above and for the following reasons.

Ho relates to water-based reactive two-part polyurethane compositions comprising a **part A** and a part B (col. 2, ll. 18 – 22), and to non-aqu ous based compositions comprising a part A and a part B (col. 4, l. 40 – col. 5, l. 34).

For aqueous-based two-part compositions, **part A** is an aqueous composition and optionally comprises

(a) urethane prepolymer having hydroxyl functionality and, optionally,

(b) a water-reducible first acrylic polymer having at least one hydroxyl group, and optionally further components (c) – (h) (col. 2, l. 38 – col. 3, l. 41).

Part B comprises a crosslinker selected from polyisocyanates, blocked polyisocyanates, and mixtures thereof (col. 3, ll. 36 – 41).

The Examiner erroneously alleges that in Example 8 and in Table 5, col. 38 Ho discloses <u>a coating composition</u> to be used as clearcoat comprising 2-butyl-2-ethyl-1,3-propanediol, an isocyanate, and two polyol compounds.

Conversely, Example 8 actually describes <u>the preparation of a PUR (polyurethane) dispersion</u> used as **component (a)** in **part A** of the two-part compositions cited above (col. 30, ll. 29 – 40). In Example 8 reference is made to the manner of Example 1. In Example 1 it is described that the reaction was allowed to run to completion [no residual isocyanate was detected by FTIR] (col. 29, ll. 14 – 16).

Ho discloses that the compositions formed by combining part A and part B can be used as coating composition (col. 23, ll. 48 – 50). **However, Ho does not disclose that the components used to prepare a polyurethane dispersion, such as the components of Table 5, can be used as a coating composition.** Applicants again respectfully request that if the Examiner maintains her objection, that she specifically demonstrate how, under the established rules for defining a coating composition, how the components in Ho (not the resultant polyurethane dispersion) can be used as a coating composition.

More particularly, we further maintain that the components of Example 8 in Table 5 **cannot be used as coating composition** as such, due to inherent instability, since they exotherm to 85°C. On the other hand, if one considers the polyurethane formed after the reaction was allowed to run to completion, it is

d plet d of isocyanate (col. 29, ll. 14 – 16) and would not have this problem. Applicants request scientific support for the Examiner's contention that inherently unstable components can be used as a coating composition.

Ho does not disclose a coating composition according to instant claim 1. Accordingly, claim 1 and all depending claims of the current application are novel over Ho.

Assuming arguendo that Ho disclosed even the polyols of instant claim1, the Examiner quotes the hydroxyl equivalent weights of the polyols used by Ho for the preparation of a polyurethane dispersion in Example 8. We presume that the Examiner is trying to demonstrate that the polyols used by Ho in Example 8 in the preparation of a PUR dispersion meet the film-forming polymer of claim 1 of the instant application. We would like to respectfully remind the Examiner that <u>a hydroxyl value expressed in mg KOH/g is different from a hydroxyl equivalent weight</u> (Nylen, Sunderland, *Modem Surface Coatings*, Interscience Publishers, 1965, p. 58, copy attached).

Polyol IV of Example 8 of Ho has a hydroxyl equivalent weight of 98 g/equivalent. 1 g of polyol IV thus contains 1/98, i.e. 0.0102 equivalents of hydroxyl groups. The equivalent weight of KOH is 56,100 mg/equivalent. In order to calculate the hydroxyl number of polyol IV one has to multiply the number of hydroxyl equivalents in 1 g of polyol, i.e. 0.0102, by the equivalent weight of KOH, i.e. 56,100. This corresponds to a hydroxyl number of 572.4 mg KOH/g of polyol IV of Example 8 of Ho.

Polyol I has a hydroxyl equivalent weight of 72.9 g/equivalent. This corresponds to a hydroxyl number of 769.5 mg KOH/g.

Thus, neither polyol IV nor polyol I, used by Ho meet the film-forming polymer of instant claim 1.

The Examiner also rejects Claims 1 – 3, 5, and 12 for alleged anticipation by Mayer. Applicants respectfully traverse this objection.

Mayer discloses a coating composition comprising a component (I) containing a binder and a component (II) containing a polyisocyanate. Component (I) comprises an acrylate copolymer and optionally a polyurethane

resin (col. 15, ll. 56 – 67). The polyurethane resin may be prepared by r acting isocyanate-containing prepolym rs with compounds, which are reactive toward isocyanate groups (col. 12, ll. 13 – 16). 2-butyl-2-ethylpropane-1,3-diol is mentioned as a suitable compound which is reactive with isocyanate groups (col. 13, ll. 15 – 23).

Mayer does not disclose a coating composition comprising a diol according to the formula of current claim 1.

Therefore, and in view of the explanation above, current claim 1 and all depending claims are not anticipated by Mayer.

Finally, the Examiner rejects claim 3 as obvious under 35 USC § 103. Applicants respectfully traverse this objection.

Claim 3 stands rejected for alleged obviousness over Ho. Ho notes the possible addition of a polyacrylate polyol to part A of the two-part composition (col. 16, ll. 18 – 34). Part A of the two-part compositions of Ho can comprise components (a) – (h) for water borne compositions (col. 2, l. 38 – col. 3, l. 18) and components (a) – (g) for non-aqueous compositions (col. 4, l. 39 – col. 5, l. 14). The optionally present polyacrylate polyol corresponds to component (b) of part A of said two-part compositions.
However, none of the components (a) – (h) and/or (a) – (g) of part A corresponds to the diol according to the formula of instant claim 1.

Furthermore, as set forth above (concerning the difference between a composition comprising a diol and a polyisocyanate and a composition comprising a polyurethane which is the reaction product of the components), it should be realized that part A of Ho's two-part composition does not comprise a diol according to the formula of instant claim 1, even if a polyurethane corresponding to component (a) is the reaction product of such a diol and isocyanates.

Accordingly, including a polyacrylate polyol in part A of the two-part composition of Ho does not lead to the composition of instant claim 3. Therefore, claim 3 is not obvious in view of Ho.

In view of the amendments and remarks herein, the papers submitted previously, the pres nt application is believed to be in condition for allowance, which action is respectfully requested.

Respectfully submitted,

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Introduction to

Paint Chemistry

and principles of paint technology

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and

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Both formerly with ICI Paints
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Fourth edition

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protects, but it rubs off. So most paints contain the second ingredient, the film-former or binder, which will be a resin or polymer, to bind together the pigment particles and hold them on the surface. If the pigment is left out, the film-former covers and protects the surface, decorating it by giving it gloss or 'sheen'. It is difficult to attach coatings that are not fluid to any but the simplest of surfaces: those that are flat or gently curving. The fluidity of paint permits penetration into the most intricate crevices. It is achieved by dissolving the film-former in a solvent, or by colloidal suspension of both pigment and film-former in a diluent. Thus the third basic ingredient of paint is a liquid. Often the film-former liquid mixture is called the vehicle for the pigment.

If the pigment is omitted, the material is usually called a varnish. The term clearcoat is used for unpigmented coatings applied over metallic paints. The pigmented varnish – the paint – is sometimes called an enamel, lacquer, finish or topcoat, meaning that it is the last coat to be applied and the one seen when the coated object is examined. Lacquers are normally thermoplastic solution paints or varnishes, but the term is sometimes (confusingly) used to describe all clear woodfinishes. Enamels are normally thermosetting paints, hard, with a superficial resemblance to vitreous enamels.

Paint applied before the topcoat is called an undercoat. Some undercoats and related finishes may be briefly defined as follows:

- Fillers or stoppers are materials of high solid content, used to fill holes and deeper irregularities and to provide a level surface for the next coat.
- Primers are applied to the filled or unfilled surface, to promote adhesion, to prevent absorption of later coats by porous surfaces and to give corrosion resistance over metals. As their name implies, they prepare the base material for further paint application. Special pigments improve the anti-corrosive properties.
- Surfacers, or undercoats in decorative house painting, are highly pigmented materials containing large quantities of extender (see below). They are easily rubbed smooth with abrasive paper. They provide the body of the paint film, level out minor irregularities in the substrate and must stick well to primer and topcoat.
- Primer-surfacers are surfacers that can be applied direct to the object's surface (the substrate), and fulfil both of the functions above in one coat.
- Sealers are clear or pigmented materials applied in thin coats to prevent the passage of substances from one coat of paint to another or from the substrate into later coats. They can be required to improve adhesion between coats, where this is otherwise weak.

All these materials are formulated on the principles described above. These are illustrated in Fig. 7.1, which also lists some of the minor ingredients of a paint. Some of the terms in the diagram need a little further explanation at this stage:

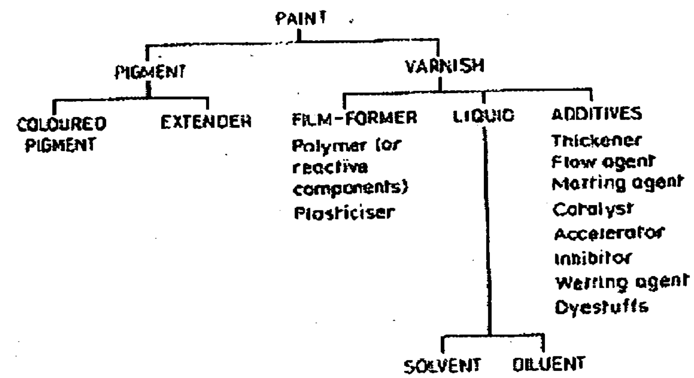

Fig. 7.1 Components of paints.

- Pigment. Any fine solid particles that do not dissolve in the varnish. If they do not provide colour they are called extender particles. Extenders are much cheaper than prime pigments and can carry out many useful functions, e.g. improvement of adhesion, ease of sanding and film strength.
- Film-former. When the coating is dry the film-former is a polymer, but in the wet sample it may be the chemical ingredients, only partly polymeric, which react to form the final dry polymer.
- Liquid. Some of the liquids of the paint are often withheld from the paint container and supplied separately as a thinner. Users add thinner to adjust the consistency to their requirements.
- Additives. Small quantities of substances added to carry out special jobs, such as the improvement of surface appearance.

Application

These are the basic ingredients, but much care in formulation will be required to produce a paint that will be easy to apply under changing conditions and pleasant to look at when dry. It is not within the aims of this book to discuss the methods of application that are available. They are well described elsewhere (see Appendix A). Suffice it to say that the paint may be put on by brushing, by roller, by a whole variety of methods of spraying (compressed air, airless, electrostatic and aerosol spraying), by dipping, electrodeposition, curtain-coating and flow-coating. Either the article is immersed in the paint, the excess of which is then allowed to drain off, or the correct quantity of paint is applied to the article and must not drain, 'run' or 'sag'.

In all cases, any irregularities in the wet film caused by the method of application must flow out to leave a smooth surface.

The first problem is to make the paint easy to handle while it is being applied. Different application methods require paints of different consistency, but in all cases the principle is the same: the greater the content of dissolved polymer in a paint, the more viscous it will be. The weight percentage of involatile material found in the paint is known as the solids content or 'solids' of the paint. Either by adjusting the 'solids' of the paint, or by altering the balance of the types of liquid used, the formulator brings the consistency or viscosity of the paint to that required.

So far so good. The difficulty lies in the next stage. Most methods of application leave some irregularities in the wet film surface: brush marks, spray mottle, roller stipple and so on. These are the methods that apply the correct amount of paint, which must flow at first to remove the irregularities, and then stop flowing, to prevent 'running' or 'sagging' of paint on vertical surfaces. This change in the rate of flow is usually brought about by evaporation of solvent, causing a rise in 'solids' and hence a thickening of the consistency. Flow dwindles until it is scarcely occurring at all. Then the drying mechanism takes over to set the film. A very careful balance of solvents is required to do this satisfactorily and more will be said about this in Chapter 9.

An alternative method, often used in conjunction with solvent evaporation, is to include some material in the paint which gives it abnormal viscosity characteristics, so that it is fluid while being agitated, but thickens up over a period when the agitation stops. This type of paint is said to be 'thixotropic'. More detail is given in Chapter 10.

If the article is allowed to drain after being coated, as in dipping, then it must drain evenly and not so rapidly that the film thickness becomes too low. If possible, thicknesses at the top and bottom of the article must vary only slightly, in spite of the downward drain of paint. Again the same principles must be used to slacken the flow.

With spray application in particular, the position is further complicated by the fact that the paint reaching the surface does not have the same composition as that leaving the spray-gun. The paint is broken up into thousands of fine droplets as it leaves the gun, each droplet presenting a surface – at which evaporation occurs – that is large compared with the droplet's volume. A great deal of liquid can be lost and this must be taken into account in formulating the paint.

It is necessary to point out that this loss of solvent – all of which has been paid for – is only accepted by the paint users on sufferance, as an inevitable consequence of the process. They are constantly looking for new materials which will contain less wasted material: in other words they want paints with higher 'solids'. Increasingly thinners other than water are all seen as hazardous to some degree and undesirable; also legislation is being enacted to reduce the amount of organic material which can be exhausted into the atmosphere, thereby polluting it. Furthermore, solvents come from petroleum, the world stocks of which are limited and must be conserved. For all

these reasons, the paint formulator chooses the ingredients to give the highest 'solids' possible.

To keep the paint manageable at high solids, the formulator has to keep the polymer molecular weight down since, as will be seen in Chapter 9, this reduces the viscosity. Alternatively (Chapter 9 again), it is necessary to take the polymer out of solution (if this is practicable and suitable) and make a dispersion or 'emulsion' paint.

Dry film properties

An outline paint formula has been described and it has been shown that application presents problems which influence the formula. After application comes drying, but before this is considered, the properties required from the dry film must be discussed, since these influence the choice of method of drying.

If the dry paint film is to be a useful one, it must stick to the surface beneath, be hard enough and flexible enough for the purpose for which it is used and must retain most of its protective and decorative properties for a long period. The paint should be capable of repair or renovation. Let us now take these requirements separately and see how they are achieved.

Adhesion

We have seen that most molecules or atoms have some attraction for one another. The strength of this attraction varies greatly with the atoms concerned, but all intermolecular attractions have one thing in common: they operate over comparatively short distances (<10 nm) and become weaker the farther apart the atoms are within that short range. At distances above 1 nm their contribution to adhesion is negligible.

Since these attractive forces are the ones that make things stick together, the first problem is to get the molecules within range, i.e. the paint film must 'wet' the surface, displacing air and all the other adsorbed materials. The critical surface tension (γ_c) of a smooth solid surface is a numerical measure of the ease of difficulty of wetting it. It is equal to the highest surface tension possessed by any liquid that will spread spontaneously when placed on it. If a paint is to wet the surface, it must have a surface tension equal to or lower than the critical surface tension of the solid. Plastics can have very low critical surface tensions (e.g. polytetrafluoroethene, PTFE = 18.5 nM m^{-1}; polyethene = 31 nM m^{-1}), which limit considerably the choice of solvents for paints to be applied to them (methods of overcoming this are disclosed in Chapter 17).

Clean metals generally have higher critical surface tensions (>73 nM m^{-1}), but even the thinnest possible layer of adsorbed oil or grease can dominate the surface (e.g. γ_c for 'clean' tinplate cans has been measured as 31 nM m^{-1}), leading to wetting problems. Even if the paint wets the contaminated surface, loosely adhering grease, dirt or rust is a menace since,

The principle of keeping the paint stable by having one reactant outside the can is quite general. Chemicals not normally in the air can be introduced into air in a confined drying chamber. This technique is used in the 'vapour curing' of isocyanate paints (Chapter 15).

Alternatively, the reactive ingredient can be in the substrate before it is coated, or in a previous coating on the substrate. This principle is used in the 'contact process' for curing unsaturated polyester coatings (Chapter 16).

The application of these separation techniques is limited only by the chemistry of individual paint systems and the imagination of paint chemists.

Drying by chemical reaction between ingredients in the paint

Obviously the paint must remain chemically stable in storage, and the reactants must not react until the paint has been applied, yet (in this method) they must all be in the paint. This paradox is resolved either by separating the reactive ingredients in two or more containers and mixing just before use or by choosing ingredients which only react at higher temperatures or when exposed to radiation of some form. The former method produces what is known as a 'two-pack paint'. Two-pack paints are less popular than their ready-mixed equivalents, because measuring is required before mixing and because of the limited period after mixing during which the paint remains usable (the 'pot life'). Sometimes two packs are avoided by so diluting the reactants with solvent that reaction proceeds only very slowly in the can, but much more quickly on a surface once the solvent has gone. Here the paint is not really stable, but a tolerable 'shelf life' is obtained. Whichever method is used, the chemical reactants may be sticky, low molecular weight polymers, or they may be simple chemicals. The reaction produces a cross-linked polymer.

Industrial stoving enamels and anti-corrosive two-pack epoxy coatings dry by chemical reaction of their ingredients.

A summary of the properties associated with the drying mechanisms is given in Table 7.1.

Relative merits

It has been shown that paints are simple in outline, but complex in operation and formulation. How can the best choice of the many ingredients available be made? The choice of pigments and solvents is discussed in the next two chapters. This summary is concerned with the film-former.

Cross-linked or not cross-linked? There are points in favour of both alternatives. The hardest, toughest, most durable and solvent-resistant films contain cross-linked polymers, and these are applied at higher solids. If they are to be matched in all respects except solvent resistance, linear polymers of high molecular weight must be used. For solution polymers,

Table 7.1 Effect of drying process on properties of paints

Method	Mol. wt of film former in can	Solids	Type of polymer film	Ease of polishing, patching and reflow	Rate of dry (no heat)	Minimum drying temperature	Handling and storage	Examples
Evaporation	High	Low, 10–35% (solution)	Linear	Good	Fast	<0°C	Good	Nitrocellulose and other lacquers
		Medium-high, 40–70% (emulsion)	Linear	Not applicable	Fast	~5°C	Good (protect water based from frost)	Decorative emulsion paints; some organosols and plastisols
Reaction between paint and (a) air	Low	Medium to high, 35–100%	Cross-linked	Fair–poor	Slow–moderate	Very slow in cold weather	Cans must be well sealed	Decorative gloss paints, some stoving enamels, one-pack polyurethanes
(b) chemicals added to air	Low				Fast	~5°C	Cans must be well sealed	One-pack polyurethanes
(c) chemicals added to substrate	Low				Fairly fast	10°C	Protect from heat	Unsaturated polyester woodfinishes
Chemical reaction between paint ingredients	Low or very low	Medium to high 30–100%	Cross-linked	Fair–poor	Can be fairly fast	Varies: 10–15°C common	Stoving and radiation curing types stable	Industrial and automotive stoving finishes; radiation curing woodfinish and overprint varnish
							Two-pack or short shelf life	Refinish 2K, acid catalysed polyurethane and polyester woodfinishes

temperature (usually 25 °C). However, viscosities read directly in viscosity units are obtained easily if the viscometer contains a paddle or disc, mechanically driven to rotate the liquid in an enclosed space. The force tending to twist the stationary part of the apparatus in contact with the liquid is usually measured and the scale is calibrated in poises or Pa s. Comparisons between measurements made in different types of instrument can then be made. Another advantage is that either the rate of shear (proportional to the speed of rotation) or the stress (proportional to the driving force) can be varied, depending on the instrument.

The second category of instrument may alternatively involve a ball falling through a liquid, or rolling in a tube containing the liquid. The time taken for movement over a given distance is measured, but conversion of the answer to poises is easily done. The liquids need to be at least partly transparent to use this type of measurement. Another type, more suitable for very viscous liquids, involves the rise of a bubble in a tube containing the liquid. The time of rise in seconds can be converted to viscosity units. This is typically used for resin solutions and frequently in resin processing. For viscous liquids there is also a method in which the vibration of a rod is damped by the liquid, the effect being related to the viscosity. Results can be obtained in poises or Pa s.

Facts and theory

There are three essential facts concerning the viscosity of a polymer solution. Let us consider them in turn.

- Early in this chapter it was stated that polymers do not have a solubility limit because they cannot crystallize. Nevertheless there are forces of attraction operating between the polymer molecules in solution. Though these forces may be weak compared with those operating in, say, a sodium chloride solution, they operate over a very long length of molecule and there are frequent encounters with other long molecules, enabling those forces to come into play. In addition, there is the possibility of simple mechanical tangling, as with pieces of string. Since both factors have been quoted in Chapter 1 as causes of increasing viscosity, it is not surprising that even comparatively low concentrations of polymer can cause considerable thickening of simple liquids. *As the 'solids' of the solution increase*, the encounters and entanglements between molecules become more frequent and *so the viscosity increases*, e.g. solution viscosities for RS $\frac{1}{2}$ second nitrocellulose (Chapter 11): 12%, 0.1 Pa s; 20%, 1 Pa s; 30%, 10 Pa s. Eventually the solution becomes so viscous that it cannot be used for paints unless further liquid is added. At higher 'solids' still, the solution almost ceases to flow and might be mistaken for a solid. So, although there is no limit at which the solution becomes saturated, there is a limit at which the solution becomes too viscous to use. No precise figure can be quoted for this, since it depends upon the use.

- If we have two solutions of the same polymer, e.g. polymethyl methacrylate, in the same solvent at the same level of solids, the more viscous solution will contain polymer molecules of higher molecular weight. Since we have the same total weight of polymer in both solutions, there are fewer polymer molecules present in the high molecular weight polymer solution, but they are longer. The increased opportunity for entanglement reinforced by chemical attraction outweighs the reduced number of molecules. All the attractions between polymer molecules in a useful solution are continuously forming and breaking with the movement of the molecules. If they were permanent, the solution would not flow, since the polymer molecules would form a semi-rigid, reinforcing network in the liquid. However, to double the molecular weight and halve the number of molecules involves making a number of these temporary associations into permanent chemical bonds. The network is not made rigid, but it is a good deal less flexible and less amenable to being deformed in flow than before. *Thus high molecular weight polymers give more viscous solutions*, e.g. 10% solutions of PVA of molecular weight 15 000, 2.5 mPa s; 73 000, 12 mPa s; 160 000, 88 mPa s.
- If we take a given sample of polymer of fixed molecular weight and dissolve it at the same 'solids' in a variety of 'true solvents', *the viscosities of the solutions will be proportional to the viscosities of the original solvents*, e.g. 12% polystyrene in methyl ethyl ketone (0.4 mPa s), 40 mPa s; in ethyl benzene (0.7 mPa s), 160 mPa s; in *o*-dichlorobenzene (1.3 mPa s), 330 mPa s. This is important, because we can reduce the paint viscosity without lowering the solids or polymer molecular weight, simply by changing to a less viscous solvent, if a suitable one is available.

Solvents in the middle 80% of the polymer's parameter range are almost certainly 'good' solvents. Good solvents dissolve the polymer at all concentrations. Some liquids ('poor' solvents) give solutions at certain concentrations, but further dilution precipitates the polymer. In these quasi-solutions, polymer molecules collect in clusters, raising the effective molecular weight of the polymer and giving an abnormally high viscosity.

It is worth noting here that if good solvents in a solution are partly replaced by non-solvents, or if poor solvent is used instead, the viscosity can rise. This happens when the average solubility parameter of the mixture moves to the extreme of the range for the polymer and clustering of polymer molecules occurs. This is the stage prior to precipitation.

Finally, a word about the viscosity of emulsions. If a polymer is fully emulsified in a liquid and no part of it is in solution, then the molecular entanglements and associations do not occur. Consequently the *emulsion viscosity must be independent of the molecular weight of the dispersed*

MODERN SURFACE COATINGS

a textbook of the chemistry and technology of paints, varnishes, and lacquers

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saponification is complete, the excess of alkali is titrated with standard aqueous hydrochloric acid in the presence of an acid/base indicator. Concurrently with this determination a blank test is carried out under identical circumstances, but in the absence of the sample. For details see B.S. 684-1958 and ASTM D 555-61.

As a measure of the content of esters in a substance, the *ester value* is sometimes quoted, this being the saponification value minus the acid value. In the presence of labile compounds such as lactones, however, the ester value becomes meaningless as a measure of ester content.

Unsaponifiable matter is oil-soluble matter that, under the test conditions, is not converted to insoluble soaps by potassium or sodium hydroxide but is soluble in the fat solvent, e.g. petroleum ether or diethyl ether used for extraction. Included in unsaponifiable matter are, *inter alia*, hydrocarbons, higher aliphatic alcohols and sterols.

Hydroxyl value is a numerical measure of the content of free hydroxyl groups in an organic substance. It is expressed as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of the substance.

In the standard method the sample is reacted with a pyridine solution of acetic anhydride which reacts according to the equation

$$ROH + \begin{matrix} CH_3OC \\ CH_3OC \end{matrix}\!\!>\!O \xrightarrow{\text{pyridine}} ROOCCH_3 + CH_3COOH$$

After acetylation is complete the excess anhydride is hydrolysed to acetic acid which is determined by titration with standard alcoholic potash solution.

Iodine value is a numerical measure of the content of ethylenically unsaturated compounds in an organic substance. It is expressed as the quantity of halogen, calculated as weight units of iodine, which 100 weight units of the substance take up under defined conditions, in other words, as the weight per cent of iodine.

A weighed quantity of the substance is dissolved in an inert solvent such as chloroform or carbon tetrachloride, and a known quantity of a reagent containing some form of free halogen (Table 3.12-2) is added in excess. After a definite reaction time a solution of potassium iodide is added and the iodine liberated by the excess of halogen is titrated with standard thiosulphate solution, using starch as indicator. A blank determination is carried out concurrently under identical conditions but omitting the sample. For details see B.S. 684-1958, ASTM D 555-61, and Gardner and Sward.[7]

There are a number of methods for the determination of iodine value which differ in the type and quantity of halogen used, in the reaction time,